DIVIDED FUEL MATERIAL AGGLOMERATED WITH A BINDER, PROCESS FOR PREPARING THE MATERIAL

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Abstract

The invention relates to a divided fuel material agglomerated with a binder, characterized in that the binder is an essentially hydrophobic thermoplastic resin containing substantially only oxygen, carbon, and hydrogen atoms. The thermoplastic resin is preferably chosen from the group consisting of polyethylenes, vinyl polymers not containing chlorine or copolymers of ethylene with vinyl monomers. The materials obtained are especially in the form of small balls, briquettes, or pellets. The agglomerated fuel materials according to the invention have an excellent mechanical behavior even during prolonged storage. The invention also applies to a process for the preparation of the said materials, characterized in that a divided fuel material and a binder are mixed and the said mixture is subjected to an agglomeration treatment.

DESCRIPTION

The present invention relates to a new combustible material agglomerated by a binder (or combustible agglomerate). It also relates to a process of preparing this agglomerate and a composition intended for the implementation of the said process.

The combustible materials appropriate for the present invention are represented by all the finely divided combustible materials usable for household or industrial purposes. In a general way, these finely divided combustible materials are selected from the substances rich in carbon, such as for example, carbon fines or dust, charcoal fines, coal coke fines, petroleum coke fines, or a mixture of these substances. These materials are abundant by-products of the modern processes of extraction and washing of coal, in particular. This is particularly related to the case of coal dust and fines.

The above materials have been utilized especially in the form of combustible agglomerates for a long time.

Various agglomeration methods of these materials, fines or dust, have been implemented industrially. Generally, these methods utilize additives or binders suitable to ensure a sufficient cohesion of the agglomerate unit.

The requirements related to the mechanical performance of these materials are very strict, taking into account the fact that the materials must be able to be stored during a very long time, possibly in open air, before a subsequent use and, nevertheless, to preserve a sufficient performance. That implies that these materials should not or should absorb little moisture, otherwise it could lead to disintegration and mould growth affecting subsequent handling.

The agglomerated materials must be manufactured by processes as simple and direct as possible, in order to avoid increasing cost of the final product. Since a large tonnage of the agglomerated materials is produced, their commercialization and profitability can not be satisfactory ensured in the case of increased expenses.

Apart from these traditional constraints, it is well known that these materials must satisfy the increasingly strict consumer requirements (pleasant aspect, non-soiling on contact), and environmental protection standards (release of emissions non-hazardous to living, vegetable or animal species).

The use of coal-tar pitch binders most commonly known today experiences a certain recession. Indeed, the agglomerate manufacturing using coal-tar pitch binders requires a thermal processing or defumigation in order to lower the concentration of phenolic compounds. Such a process results in a high atmospheric pollution. Moreover, if the defumigation is not complete, the combustion of these agglomerates will unavoidably release emissions hazardous to living species. Certain countries have already prohibited the use of the combustible agglomerates containing coal-tar pitch.

The same disadvantages are known when coal-tar pitch is replaced by bitumen.

In order to mitigate these disadvantages, it was proposed to replace the aforementioned binders by lignosulfonates, especially by ammonium lignosulfonates. The use of these agglomerates was described by many documents, for example, by patents SU 983.147, SU 1 010 146, SU 1 137 103, EP 0 097 486, DE 3227395, DD 224331, and US 4666522.

Unfortunately, the industrial manufacturing of this type of agglomerates is very complex, and consequently, generates significant expenses.

According to such a process, the following stages are required:

- drying the fines to attain a precise moisture level so that the fines-binder mixture can be agglomerated. The agglomeration is impossible if the moisture level is lower or higher than required;

- polymerizing the lignosulfonates according to a certain temperature profile in order to render them insoluble, and thus, imply good water resistance to the agglomerate.

However, the temperatures necessary to insolubilize the agglomerates are very high, being, especially, in the range from 270 to 450 °C depending on the nature of the lignosulfonates employed, while the heat treatment can require more than 3 hours.

In addition, this method is also very polluting owing to the hazardous emissions rich in sulfuric acid released during the thermal processing.

Setting-up installations for condensation of the emissions downstream from the thermal processing is also not sufficient. In this case, the problem of pollution is simply replaced by the problem of corrosion that is also difficult to solve, especially when it is necessary to treat a condensate rich in sulfuric acid. Thus, the use of lignosulfonates is also associated with additional expenses.

It also should be noted that the use of lignosulfonate binders presents an additional disadvantage, since sulfur residues are released in the combustion emissions.

In order to avoid the aforementioned disadvantages, other processes were proposed in which pitch, tar, or lignosulfonates are replaced by clays, for example, bentonite. Such processes are particularly described in the patents US 4025596 and DE 1671365. Though the problems of air pollution are solved by the use of these binders, the obtained agglomerates do not possess all the necessary physical characteristics. In particular, their mechanical and water resistance is poor. As a consequence, these processes have not been adopted by the industry.

One also proposed to use starch as a binder, alone or in mixture with other binders. Such methods described in the patents US 3726852 and DE 3227395 or patent EP 0097486 have many advantages, so much on the level of the implementation (the starch does not require special precautions with regard to the moisture of fines-binder pre-mixture produced before the agglomeration), as well as on the level of the mechanical properties of the agglomerates obtained by the process (resistance to mechanical compression, to abrasion, and impact).

From the industrial standpoint, starch has an additional advantage that allows it to be used in installations initially designed for the use of pitch or bitumen. Thus, its use does not require an additional investment, which reduces the maintenance cost of the installations.

Lastly, the combustion of these agglomerates does not lead to toxic or polluting emissions. However, the starch agglomerates have a major disadvantage of being very sensitive to water, making impossible their storage in a wet atmosphere, especially, in outdoors.

Mixing starch with coal-tar pitch, asphalt or bitumen or rendering starch insoluble using the resins of urea, phenol-formaldehyde, melamine- formaldehyde, ketone-formaldehyde, or their mixture, also does not constitute a satisfactory solution because of the aforementioned problems related to the polluting emissions.

At the same time, the addition of organosilicon waterproofing agents to the binder as proposed in the patent FR 88 00219, results in additional expenses. Moreover, it was noted that the obtained agglomerates were still highly water sensitive.

It appears that none of the combustible agglomerates obtained by the earlier processes satisfies the various criteria mentioned at the beginning this review.

Thus, one of the objects of this invention relates to new combustible materials agglomerated by a binder displaying an excellent mechanical performance during prolonged storage, even in wet atmosphere. In particular, these materials are not or little susceptible to the growth of mould, even at the aforementioned storage conditions.

Another object of this invention is a combustible material agglomerated by a binder that does not release polluting and/or hazardous emissions during combustion.

Another object of this invention is a combustible material agglomerated by a binder whose manufacture can be industrially implemented without additional stage or condition involving significant extra costs.

Other advantages and objects of this invention will be apparent during the following description.

The present invention relates in the first place to a divided combustible material, agglomerated by a binder, characterized in that the binder is an essentially hydrophobic thermoplastic resin.

The combustible materials usable within the framework of this invention are those which were mentioned in the introduction above. They are substances rich in carbon, such as, for example, coal dust or fines, but also charcoal fines, coal coke fines, petroleum coke fines, or a mixture of these products. In general, the invention is not limited to this type of materials and extends to all similar combustible materials likely to be agglomerated.

Surprisingly, it was found that a binder based on an essentially hydrophobic thermoplastic resin made it possible to obtain agglomerates having all the necessary qualities mentioned above, especially in what is related to the mechanical performance, water resistance, and nonpolluting emissions.

To avoid the release of polluting emissions, these resins should not contain substantial amounts of chlorine or sulfur.

The essentially hydrophobic thermoplastic resins usable within the framework of this invention contain substantially only the atoms of carbon, hydrogen and of oxygen, and preferably are obtained by polymerization of ethylene monomers.

These resins are well known to those skilled in the art.

Among these resins, it is preferable to use those chosen from the group consisting of polyethylenes or non-chlorinated vinyl polymers, such as polyvinyl acetates, or a mixture of those. It is also possible to use copolymers made of vinyl monomers and ethylene, such as ethylene vinyl acetate copolymers.

It is even more preferable to use a polymer chosen from the group consisting of polyvinyl acetate, ethylene vinyl acetate copolymers, or a mixture of those.

The binder is distributed homogeneously within the mass of divided combustible material. The ratio of binder relative to combustible material must be sufficient to allow the resulting combustible agglomerate to resist water and the elements, and additionally, to satisfy the common requirements of mechanical performance well known in art.

The combustible material according to the invention can also include other components or fillers, for example, carbonates, the quicklime or lime, dolomite, alkaline silicates, clays, latexes, polyphosphates, phosphates, cement, and polyvinyl alcohols. These loads should not affect the essentially hydrophobic character of the binder.

The material can also include odor-masking agents and perfumes added to improve the olfactive presentation of materials.

In general, the proportion of such components can reach 20 % by weight relative to the weight of the divided material. The size distribution of these components must be preferably close to that of the divided material.

According to the present invention, the size of the divided combustible material that represents the main component entering the agglomerated material in a predominant amount generally lies in the range from 1 micrometer to approximately 1 centimeter.

Preferably, the weight ratio of the binder to combustible material is in the range from 0.1 to 30 %, preferably from 0.5 to 20 %. More preferably, this ratio will be in the range from 1 to 10 %, preferably equal or lower than 5 %.

The object of the invention is also represented by divided combustible materials agglomerated by a binder and presented in the form of balls, briquettes, or pellets.

The invention also relates to a process of manufacturing divided combustible materials agglomerated by a binder, the process characterized by mixing a combustible material

divided such as defined previously and a binder, possibly in the presence of one or more components or odor masking agents or perfumes as previously described, and then subjecting the said mixture to an agglomeration process.

The binder can be mixed in a kneader in solid, melted, aqueous form (emulsion or dispersion), or in solution with an organic solvent. In the case of the aqueous formulations, it is preferable to add an additional quantity of water.

The mixture is generally prepared at ambient temperature or a temperature lower than 150 °C, preferably lower than 100 °C. The temperature of kneading is mainly a function of the binder nature and composition.

Preferably, polyvinyl acetate binder will be in the form of an aqueous emulsion having the weight proportion of solids and emulsion between 5 and 95 %, preferably, between 10 and 75 %.

The agglomeration methods utilized in the said process are commonly selected from the group comprising pelletization, pressure-compaction, extrusion, or molding.

According to another embodiment of the process of the invention, the obtained agglomerate is subjected to a heat treatment in the temperature range from approximately 80 - 100 °C to approximately 180 °C. It is also possible, although not strictly necessary, to cover the surface of agglomerates with a protective film or strip in order to further improve their abrasion resistance and limit the generation of fines during handling.

To apply the aforementioned protective film, one of the products chosen from the group consisting of acrylic, polyvinylic and ethylene derivatives, alkaline silicates, salts of phosphate, cellulose derivatives, styrene-butadiene resins, and sulfate liquors can be utilized. Preferably, this film can be pigmented by incorporation of a nontoxic organic or mineral pigment.

The invention also relates to a composition created to implement the said process comprising a binder as defined above, a finely divided combustible material, and various fillers and/or odor masking agents. The preferable embodiments indicated in the description of the process are also applicable to the aforementioned composition (especially to the binder nature and ratio).

The invention could be better understood using the following example of a preferred embodiment.

EXAMPLE

Balls made of coal fines

To 20 kg of coal fines having 2 % surface moisture and sized in the range from 0 to 6 mm, 800 gram of polyvinyl acetate emulsion containing 50 % solids by weight is added in a kneader.

After adding 0.500 Liter of water, the obtained mixture is kneaded at ambient temperature for 5 minutes.

The mixture is agglomerated by pressure-compaction on a ball press, whose linear pressure (*precision* in the French original) is adjusted to 16.7×10^5 N/m.

Thus, the coal balls are obtained that without further treatment (green) have a cohesion sufficient to withstand transportation

The balls have a good mechanical resistance after 1 hour of drying at ambient temperature.

The resistance of the balls determined using a CERCHAR type press is as follows:

- green (without further treatment)	1.5 MPa (15 bar)
- after 24 hour of drying at ambient temperature	3 MPa (30 bar)
- after heat treatment for 1.5 hour at 130 °C	15 MPa (150 bar).

The balls are then immersed in cold water. Disintegration is not observed even after several months of immersion.

The mechanical resistance of the balls remains unchanged after the stay in water and a simple draining.

In addition, if subjected to a biological inoculation (bacterium, mould) in wet atmosphere at the temperature of 35 °C, the agglomerated and heat treated balls do not display a visible growth of the seeded colonies.

This example shows that the substitution of the common binders used for the agglomeration of coal fines by a polymeric binder described in the present invention, and especially, by polyvinyl acetate binder, dosed as polyvinyl acetate emulsion at 4% relatively to the weight of combustible fines, allows to obtain agglomerates meeting the technical requirements (mechanical resistance, water resistance, long term storage while exposed to the weather elements) and the requirements of environmental protection (absence of pollution during manufacture, storage, and use of the said agglomerates).

CLAIMS

1. Combustible material, divided, agglomerated by a binder, characterized in that the binder is an essentially hydrophobic thermoplastic resin containing substantially only atoms of carbon, oxygen, or hydrogen.

2. Material according to Claim 1, characterized in that the thermoplastic resin is selected from the group consisting of polyethylenes, vinyl polymers not containing chlorine, copolymers of ethylene with vinyl monomers, or the mixtures of those.

3. Material according to Claim 2, characterized in that the vinyl polymer is selected from the group consisting of polyvinyl acetate, ethylene vinyl acetate copolymers, or a mixture of those.

4. Material according to Claim 1, characterized in that it also comprises fillers and/or agents masking odor.

5. Material according to Claim 1, characterized in that the weight ratio of the binder to the combustible material is in the range from 0.1 and 30 %, preferably in the range from 0.5 to 20 %.

6. Material according to Claim 5, characterized in that the weight ratio of the binder to the combustible material is in the range from 1 and 10 %, preferably equal or lower than 5 %.

7. Material according to one of the preceding claims, in the form of balls, briquettes, or pellets.

8. Manufacturing process of materials according to one of Claims 1 to 7, characterized in that a divided combustible material is mixed with a binder, and then the said mixture is subjected to an agglomeration process.

9. Process according to Claim 8, characterized in that the binder is mixed in solid form, melted, aqueous (emulsion or dispersion) or in solution (organic solvent).

10. Process according to the Claim 9, characterized in that the binder is an aqueous emulsion of polyvinyl acetate in which the weight proportion of solids and emulsion is in the range from 5 to 95 %, preferably, from 10 to 75 %.

11. Process according to Claim 8, characterized in that an odor masking agent is added to the mixture before agglomeration.

12. Process according to Claim 8, characterized in that the mixture is prepared in the temperature range from ambient to 100 °C.

13. Process according to Claim 8, characterized in that the mixture is agglomerated by pressure-compaction, pelletization, extrusion, or their combination.

14. Process according to one of the preceding claims, characterized in that the agglomerate obtained at the end of agglomeration is subjected to a heat treatment generally in the range from 80-100 °C to approximately 180 °C.

15. Composition created to implement the process according to one of Claims 8 to 14, characterized in that it consists of a divided combustible material, binder according to one of Claims 1 to 3 and 5 and 6, and possibly, fillers and/or odor masking agents.